

Automated Trace Metal Analyses of Slurried Samples by Graphite Furnace Atomic Absorption Spectrometry*

Application Note

Atomic Absorption

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Introduction

Compared to the analysis of dissolved samples, solid sampling followed by electrothermal atomic absorption spectrometry (EAAS) offers two advantages. First, it saves time and effort for samples that are difficult to dissolve. Second, solid sampling may be particularly convenient when only small amounts of sample are available.

However, direct analysis of solid samples by EAAS is initially handicapped due to some restrictive factors not present in the analysis of dissolved samples:

- The greatest problem originates from sample heterogeneity which requires a substantial effort to obtain representative subsamples.
- Determination of relatively high analyte concentrations is limited by the minimum representative sample weight, obtained with a current analytical balance, that can be introduced into the atomizer.
- One of the major difficulties associated with solid sampling concerns the availability of appropriate calibration standards.
- For multi-element analysis this technique is particularly time-consuming compared to the work with solutions.
- The interference effects observed with solid sampling are probably greater compared to the dissolved sample.
- Good contact between the analyte and the graphite surface necessary for reproducible heat transfer from platform to analyte and for the possible analyte reduction prior to the atomization cannot be ensured.
- The use of matrix modifiers, often required to achieve the efficiency of platform techniques, is problematic.
- Sample introduction into the atomizer is less convenient compared to dissolved sample.

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Finally, for all the reasons mentioned above the analytical precision obtained by solid sampling is generally not as good as that obtained with solution analysis.

In spite of this discouraging situation, many researchers consider that solid sampling facilitates analysis in some specific cases and may lead to consistent results. A possible alternative to solid sampling is dispensing of liquid-suspended powdered sample directly into the atomizer.

We investigated this approach and found that it offered advantages compared to true solid sampling. The recent evolution of ET-AAS using platforms, modifiers, autosamplers and adequate signal processing contribute largely to routine applications of this solid sampling alternative.

These advantages can be summarized as follows :

- With the use of autosampler, automation is always possible.
- The dilution of slurries or the dispensing of smaller volumes make it easier to determine relatively high analyte concentrations.
- The addition of modifiers and use of the standard additions method is much more straightforward.
- Sample introduction is easy compared with true solid sampling.
- The analytical speed is the same as with solutions.
- Finally, a sequential multi-element analysis is possible for the same suspended sample.

Experimental

All work was performed on a Varian SpectrAA-10 spectrometer equipped with a deuterium background corrector, GTA-96 graphite furnace, and programmable sample dispenser.

Pyrolytically coated tubes and solid pyrolytic graphite platforms were used.

Appropriate amounts of the powdered sample were weighed with an analytical balance (Mettler H-74, precision 0.01 mg) in 2-mL polyethylene microvials for autosampler.

A Hewlett-Packard 82905-A printer was used for plotting absorbance-time profiles. Signal processing was in the peak-height mode.

The complex liquid media were prepared with glycerine (87% Merck p.a.), methanol (Baker p.a.), HNO_3 (65%, suprapur Merck) and appropriate matrix modifiers (Pd, Pr Specpure Johnson & Matthey). The metal standards were diluted from commercial standard solutions (Tritisol, Merck). Preparation

of the liquid media and dilutions of the standards and the modifiers were performed with a Hamilton Microlab 1000 diluter or Gilson micropipets.

Results and Discussion

With suspended solid samples it is first necessary to ensure sufficient homogeneity and stability of the particles in the liquid medium (Figure 1). We have tested different types of powdered solids : plant and animal tissues, soil and sediment samples.

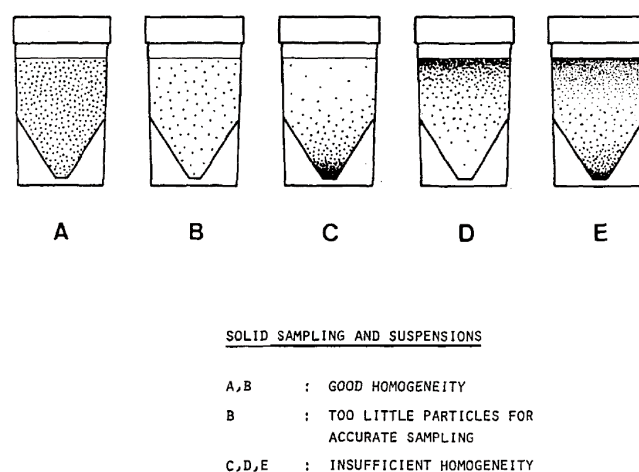


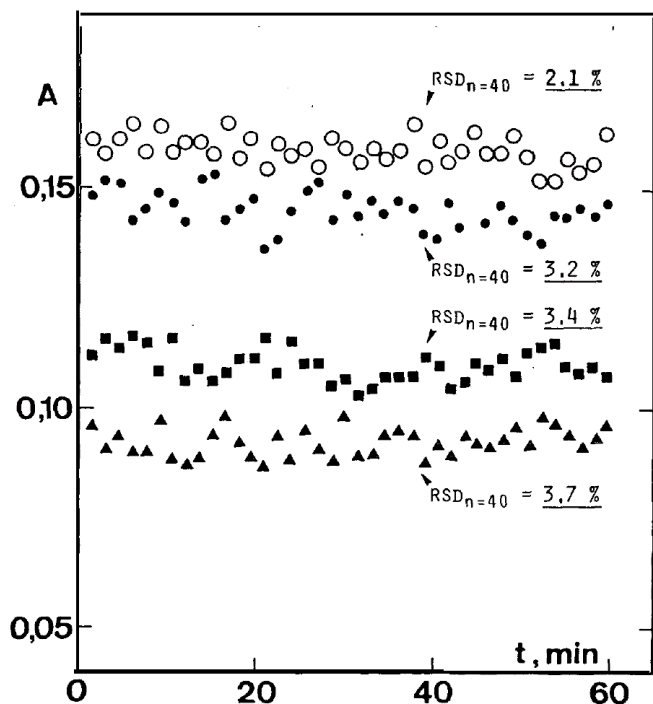
Figure 1. Solid sampling and suspensions.

We tried to produce a liquid medium that would give satisfactory reproducibilities for suspensions having different matrices.

The samples were first suspended in demineralized water. In this medium, all samples showed rapid sedimentation. The lead determinations performed on aliquots of these suspensions showed a strong decrease of atomic signal with time. Ten minutes after sample stirring, the lead absorbance signal decreased by about 60% for the sediment sample and between 10 and 20% for animal and plant samples, due to particle sedimentation.

Acceptable results with water suspended samples can be obtained if the suspension is stirred periodically just before sampling. However, this alternative is not compatible with automation of the procedure.

Preliminary tests have shown that the viscosity of glycerine kept the different types of particles in suspension for a sufficient period. An example for cadmium is illustrated in Figure 2. Furthermore, the decomposition of the glycerine, accompanied by heavy smoke, is achieved during the ashing step and no significant background signal is generated during the atomization step.



- AQUEOUS STANDARD WITH GLYCERINE (3 NG.ML⁻¹ Cd)
- LYOPHYLIZED ANIMAL TISSUE
- PLANT SAMPLE
- ▲ MARINE SEDIMENT

Figure 2. Repeatability test for cadmium (5 µ sampling).

For plant and sediment samples the best results were obtained with ratios 2 + 1 and 4 + 1 of glycerine+demineralized water. These amounts are not critical and changes of these parameters do not influence the quality of the analysis.

However, lyophilized animal tissue particles agglomerate in this medium. Their dispersion was achieved by using methanol instead of demineralized water.

Appropriate modifiers were added directly to this liquid medium or added separately using the autosampler.

To compensate for differences in viscosities when dispensing standards and samples, we also added glycerine to the aqueous standards.

The appropriate amounts of the sample were weighed directly in the autosampler microvials. After addition of 1 mL of liquid medium, the slurries were homogenized with a mini-stirrer prior to the analysis. The suspended samples were then dispensed by autosampler capillary on the tube wail or platform.

The following elements were determined: cadmium, lead, copper, chromium and cobalt.

Results for cadmium are presented in Table 1. They show that with the applied furnace program, peak height mode, platform atomization and palladium modifier the curve slopes are very similar for the matrices studied. The direct calibration is then valid. The results show the reliability of the whole analytical approach.

Table 1. Cadmium (228.8 nm)

Furnace program	800/1800, platform	
Modifier	Pd (8 µg/10 µL sample)	
Measurement mode	Peak height, direct calibration	
Sample	Value found µg/g	Recommended value µg/g
Aqueous standard		
NBS citr. leaves	0.028	0.03 ± 0.01
NBS orch. leaves	0.101	0.11 ± 0.01
NBS bovine liver	0.304	0.27 ± 0.04
IAEA fish homg.	0.062	0.066 ± 0.004
NBS estuary sod.	0.420	0.36 ± 0.07
Curve slope range	18.7 to 19.2 A/ng	
Precision range	3 to 25 %RSD (n = 5)	

The case of lead is similar (Table 2): direct calibration leads to consistent results. The effect of the palladium modifier is illustrated in Figure 3.

Table 2. Lead (283.3 nm)

Furnace program	900/2200, platform	
Modifier	Pd (8 µg/10 µL sample)	
Measurement mode	Peak height, direct calibration	
Sample	Value found µg/g	Recommended value µg/g
Aqueous standard		
NBS spinach	1.42	1.2 ± 0.2
NBS tom. leaves	6.62	6.3 ± 0.3
NBS pine needles	11.4	10.8 ± 0.5
NBS bovine liver	0.38	0.34 ± 0.08
IAEA fish homg.	0.51	0.58 ± 0.07
NBS estuary sed.	29.2	28.2 ± 1.8
Curve slope range	0.81 to 0.83 A/ng	
Precision range	3 to 15 %RSD (n = 5)	

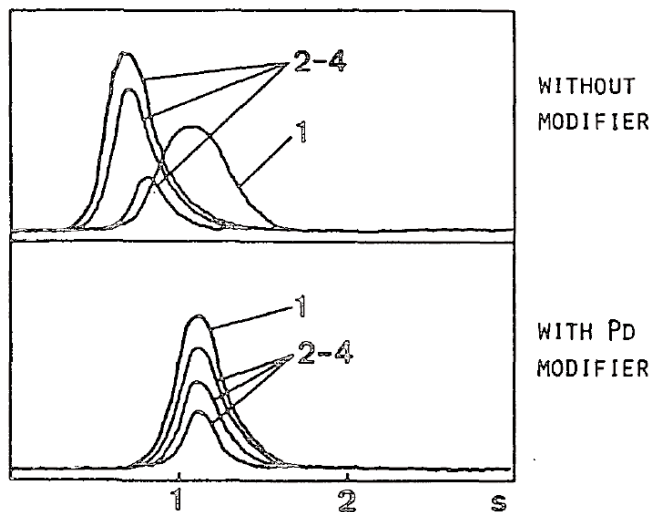


Figure 3. Absorbance-time profiles for lead in aqueous standard (1) and the different matrices studied: sediment, animal and plant tissues (2-4); platform atomization.

The copper results are presented in Table 3. In this case, the direct calibration method is possible using palladium modifier. Table 4 shows that the direct calibration with aqueous standard is also possible for chromium using platinum-palladium mixed modifier. The absorbance-time profiles are shown in Figure 4.

Table 3. Copper (327.4 nm)

Furnace program	1100/2600, platform	
Modifier	Pd (8 µg/10 µL sample)	
Measurement mode	Peak height, direct calibration	
Sample	Value found µg/g	Recommended value µg/g
Aqueous standard		
IAEA soil -7	9.1	11 ± 2
IAEA mussel	8.2	8 ± 0.5
NBS estuary sed.	20.6	18 ± 3
NBS citr. leaves	14.6	16.5 ± 1
NBS pine needles	3.5	3.0 ± 0.3
Curve slope range	0.5 to 0.6 A/ng	
Precision range	3 to 12%RSD (n = 5)	

Table 4. Copper (327.4 nm)

Furnace program	1100/2600, wall	
Modifier	Pd (8 µg/10 µL sample)	
Measurement mode	Peak height, direct calibration	
Sample	Value found µg/g	Recommended value µg/g
Aqueous standard		
IAEA soil -7	58.2	(60)
NBS pine needles	2.1	2.6 ± 0.2
IAEA mussel	0.93	(1.25)
NBS citr. leaves	0.80	0.8 ± 0.2
Curve slope range	3.2 to 3.5 A/ng	
Precision range	5 to 20 %RSD (n = 5)	

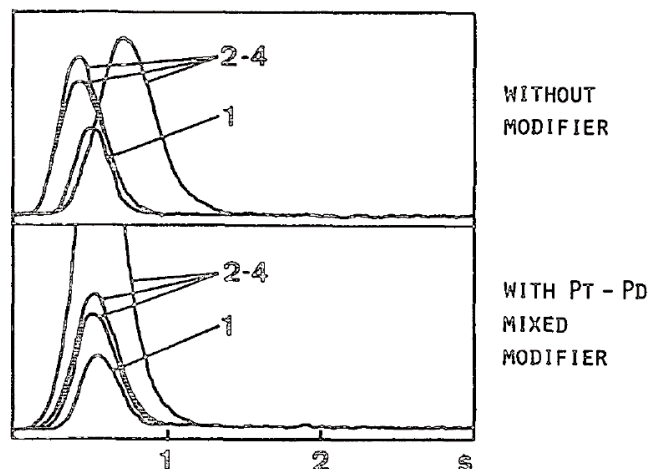


Figure 4. Absorbance-time profiles for chromium in aqueous standard (1) and the different matrices studied: soil, animal and plant tissues (2-4); wall atomization.

The worst case observed was for cobalt (Table 5): the curve slopes in aqueous standards and samples are different, even using platinum-palladium mixed modifier. In this case the standard additions method must be used and the agreement with recommended values is good. The complexity of the modifier choice is shown in Figure 5.

Table 5. Cobalt (240.7 nm)

Furnace program	850/2300, wall		
Modifier	Pt (1.5ng) + Pd (4.5 ng); 3–5 μ L sample		
Measurement mode	Peak height, direct additions		
Sample	Curve slope A/ng	Value found μ g/g	Recommended value μ g/g
Aqueous standard	1.36		
IAEA Soil -7	1.21	11.4	(8.9)
IAEA Soil -5	1.21	13.1	14.8 \pm 0.8
IAEA Marine sed.	1.21	12.2	12.1 \pm 0.5
NBS Estuary sed.	0.92	9.8	10.5 \pm 1.3
Precision range	3 to 10 %RSD (n = 5)		

Conclusions

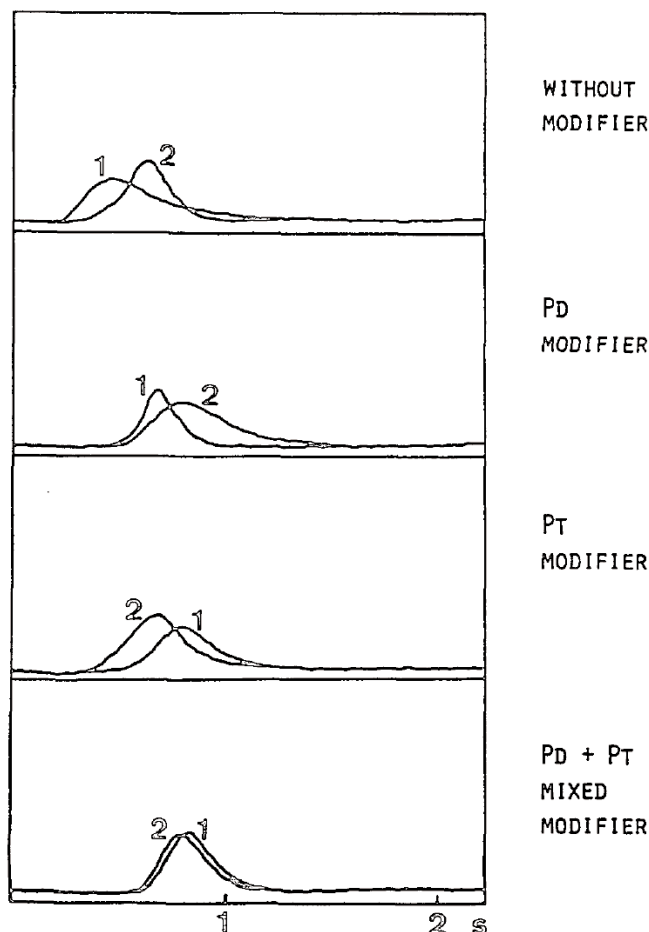


Figure 5. Cobalt: Modifier Study Absorbance-time profiles in aqueous standard.

Conclusion

With direct dispensing of slurries on the platform or tube wall, the determination of trace elements in some matrices is rapid and easy.

It is evident that the procedure described may be employed for other elements and matrices using appropriate modifiers. Excessive background signals were not observed. The background levels were not significantly higher than those observed when analyzing corresponding sample solutions. They range between 0 and 0.3 absorbance (easily corrected by a deuterium device).

The integrated absorbance is, in principle, more suitable for an appropriate quantification. This work shows that the peak height measurements can also lead, under controlled conditions, to consistent results. The accuracies obtained and the rapidity of the technique permit the analysis of solid samples on a routine basis.

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